CH 302 – Unit 1

EXAM REVIEW: PHYSICAL EQUILIBRIA

http://mccord.cm.utexas.edu/courses/spring2018/ch302/exam1.php

Unit One Road Map

Jimmy Wadman on Spotify:

The theme of Unit One is the thermodynamics of phase changes and how creating a solution increases the stability of the liquid phase

1. Quantifying phase changes using enthalpy, entropy, and free energy
2. Heat exchange between system and surrounding of physical and chemical changes
3. Vapor Pressure: concepts, calculations, and its relationship to boiling and IMFs
4. Phase Diagrams: showing the most stable phase of a substance at a given temperature and pressure
5. Thermodynamics associated with creating a solution
   - Does it dissolve?
   - Temperature dependence
6. Colligative Properties: the increased stability of a solution changes the physical properties accordingly
   - Vapor pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure
7. Percent Ionization of weak electrolytes ("non-ideal" solutions)

horizon of victory

Exosuit
Epic North • Mammoth

This Is the Future
Epic North • Viking Warriors from Outer Space

Guardians At the Gate
Audiomachine • Chronicles

Th3 Awak3n1ng
Really Slow Motion • Fiery the Angels Rose

Common Errors

- Forgetting or misusing *i* (van't Hoff Factor) in colligative property calculations, concepts
- Not knowing how to convert between concentration units
- Mixing different units without converting (particularly with osmotic pressure, CC equation)
- Forgetting to study the underlying thermodynamics of phase changes, dissolution
- Forgetting to study the importance of stoichiometry: conversions between concentration units, moles, and molecular weight

Phase Changes

EQUILIBRIUM CALCULATIONS, HEATING CURVES, PHASE DIAGRAMS

Free Energy and Spontaneity

- **The equation we will use to determine the spontaneity of a reaction is:**

$$\Delta G = \Delta H - T\Delta S$$

- This law gives us three conditions for **ΔG_{rxn}**:
  1. $\Delta G < 0$ (negative) ; your reaction is spontaneous
  2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium
  3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous

Summary: you have a finite energy in the universe. Any reaction that happens spontaneously will lower the amount of "free energy" in the universe (negative ΔG).

Free Energy: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

Freezing, condensation, deposition

Energy OUT = lower entropy, energy state
Exothermic, so the phase change gives its energy to the surroundings

Fusion (melting), boiling, sublimation

Energy IN = Higher entropy, energy state
Endothermic, so we get the energy to do this phase change from the surroundings

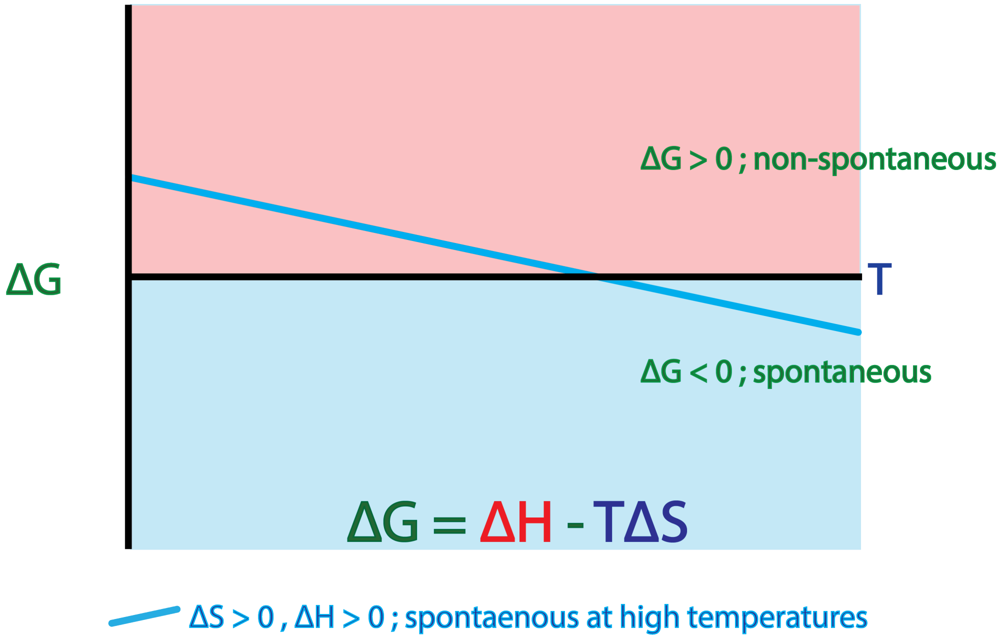
Melting, Boiling, Sublimation

- **Each of these phase changes has (+)ΔH and (+)ΔS**

$$\Delta G = \Delta H - T\Delta S$$

What do the signs of ΔG mean?

1. ΔG < 0 (negative) ; your reaction is spontaneous, the temperature is high enough
2. ΔG = 0 (zero) ; your reaction is at equilibrium, the temperature = T_{trans}
3. ΔG > 0 (positive) ; your reaction is nonspontaneous, the temperature is too low



Freezing, Condensation, Deposition

- **Each of these phase changes has (-)ΔH and (-)ΔS**

$$\Delta G = \Delta H - T\Delta S$$

What do the signs of ΔG mean?

1. ΔG < 0 (negative) ; your reaction is spontaneous, the temperature is low enough
2. ΔG = 0 (zero) ; your reaction is at equilibrium, the temperature = T_{trans}
3. ΔG > 0 (positive) ; your reaction is nonspontaneous, the temperature is too high

Summary: Temperature is the “balance” between a phase change that is spontaneous or non-spontaneous. Whether you want temperature to be high or low depends on the signs of ΔH, ΔS

Heat Transfer of Physical Changes

We have two ways of calculating the heat transfer at constant pressure.

$$q = mC_s\Delta T$$

One phase, change in temperature

$$q = m\Delta H_{trans}$$

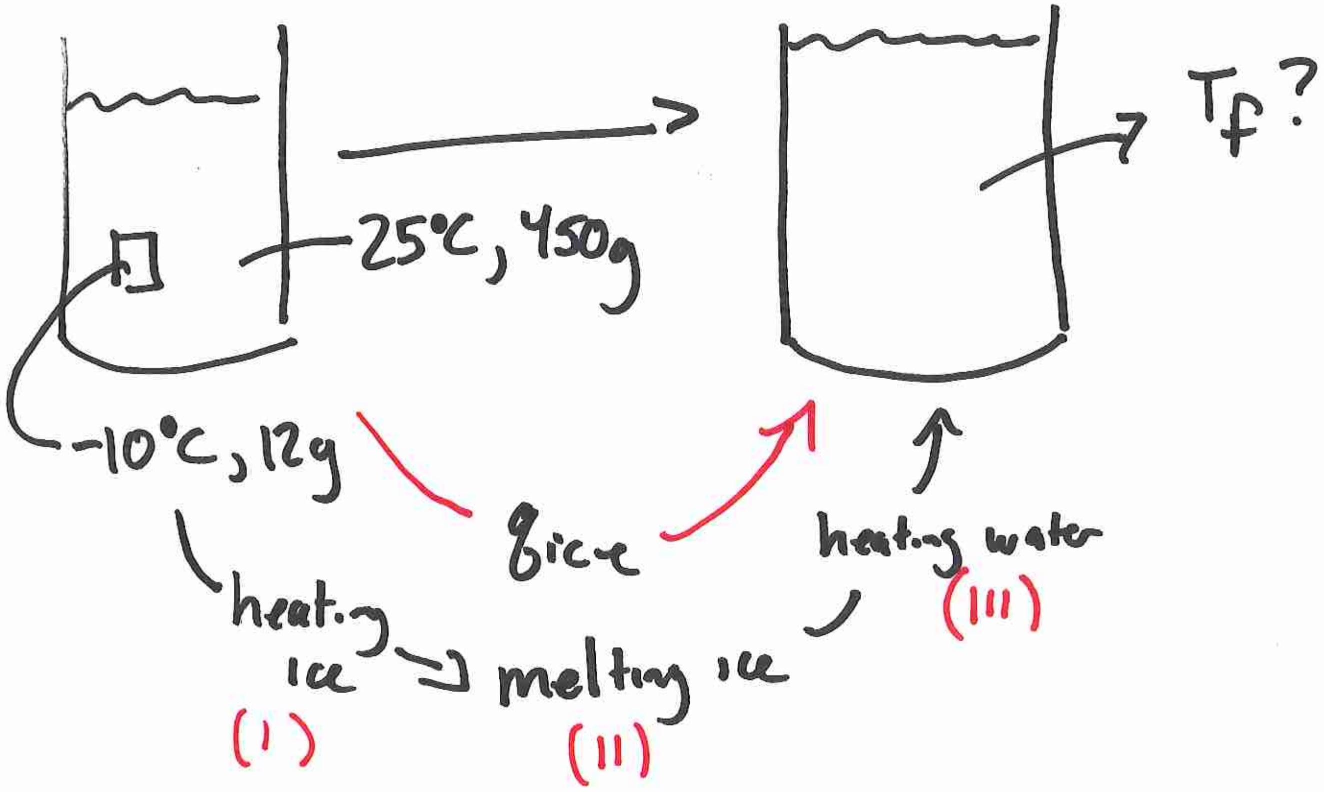
Two phases, no change in temperature

We typically measure these quantities by the transfer of heat to the surroundings:

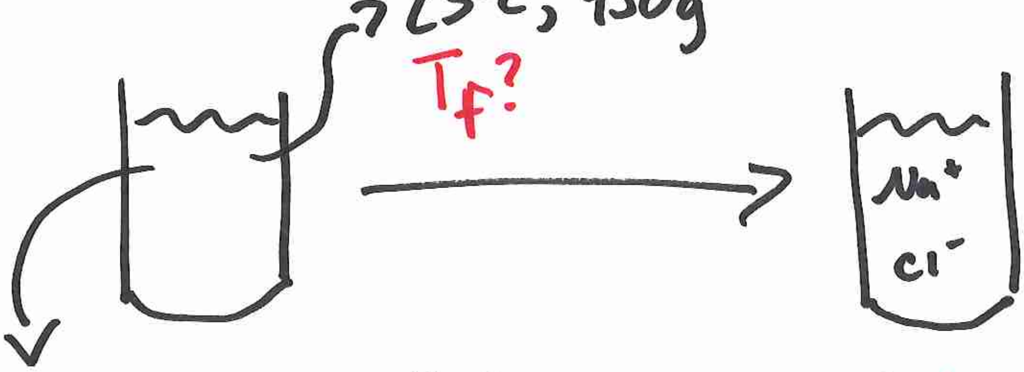
$$q_{sys} = -q_{surr}$$

This is a simplified look at how we measure heat transfer for phase changes and dissolution reactions.

$q_{ice} = -q_{surrounding\ H_2O}$



$$\underset{(I)}{mC_{ice}\Delta T} + \underset{(II)}{m\Delta H_{fus}} + \underset{(III)}{mC_{water}\underset{\boxed{T_f}-T_i}{\Delta T}} = -mC_{surr}\underset{T_f-T_i}{\Delta T}$$



10g NaCl, $\Delta H_{sol} = 3.9\ kJ/mol$

$m\Delta H_{sol} = -mC_{H_2O}\Delta T$

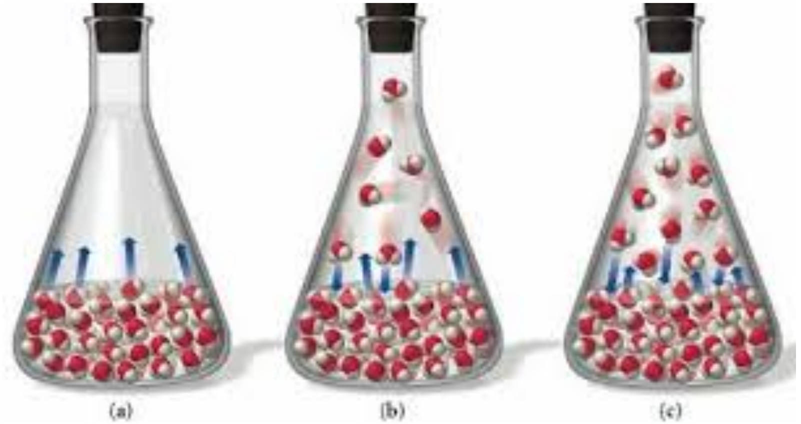
Vapor Pressure

CONCEPTS, BOILING, CALCULATIONS

SEE REVIEW 1 FOR GOOD QUESTIONS

Vapor Pressure

- For any given liquid sample in a closed container, a certain amount of that sample exists is the gas phase. This is what is known as the **vapor pressure**.
- **These molecules have enough kinetic energy to "escape" the attractions of other molecules on the surface.**
- Vapor pressure is a function of dynamic equilibrium between the gas and the surface molecules of a liquid.



- The Vapor Pressure is a function of **the IMF's of the liquid** and **the temperature.**

Don't Forget: A "lowered" vapor pressure follows these rules. For a solution vs. pure solvent, the solution has a more stable liquid phase and a higher T_b

Vapor Pressure and IMF's

- If Vapor Pressure is the pressure of gas above a liquid in a closed container at a given temperature, we can easily determine that a sample with High IMF's will have a Low VP (less molecules able to overcome the IMFs and be "lifted into the gas phase).

Strong IMF - > low VP (and high boiling point, high ΔH_{vap})

Weak IMF -> high VP (and low boiling point, low ΔH_{vap})

IMF Review

Dispersion Forces < Dipole Forces < Hydrogen-Bonding

Dispersion forces:

C_nH_{n+2}, CCl_4, $C0_2$, F_2 etc.

Dipole-Dipole:

CH_2O, CH_3COCH_3, $AsCl_3$, etc.

H-bonding:

CH_3OH, H_2O, HF, NH_3, etc.

Important point: when the vapor pressure is equal to the atmospheric pressure (1 atm or 760 torr), what is the temperature equal to for that liquid? The normal boiling point.

Vapor Pressure Calculations

- Mathematically, the vapor pressure for a given liquid is only dependent on a change in temperature.

Higher Temperature = Exponentially Higher Vapor Pressure $P_{vap} = K \cdot e^{\frac{-\Delta H^{\circ}_{vap}}{R \cdot T}}$

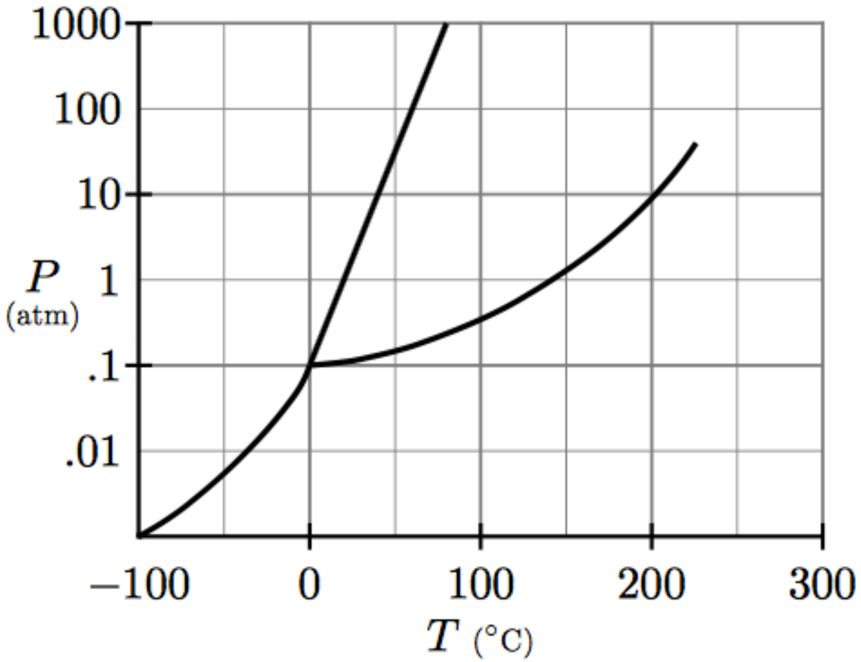
- **Changing the surface area, size of the container, amount of water, and so on does not change the pressure.**
- Of all the derivations used to model this relationship, the most important equation to you will be the Clausius-Clapeyron Equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note: the order of P_2 / P_1 and $(1 / T_1 - 1/T_2)$ is important. If you forget the order, remember that as you increase temperature, you are increasing vapor pressure. You are taking the difference of the inverse temperature, so you need to switch the order.

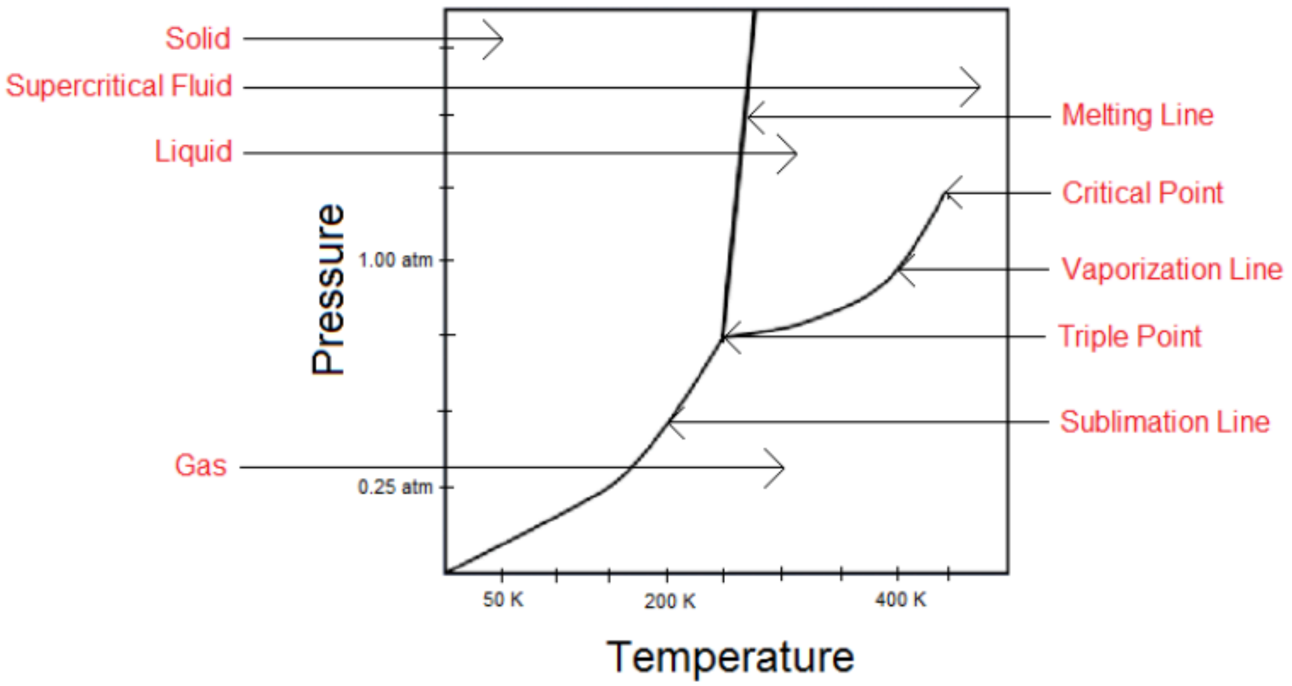
Phase Diagram Checklist

- Phase diagrams show the lowest free energy phase (most stable) of a substance at a given temperature and pressure.
- Identify the key features of the diagram:
  - What is the stable phase at a certain temperature and pressure?
  - Identify the triple point
  - Identify the critical point
  - What phase transition does a specific line represent?
  - What is the meaning of the solid-liquid line’s slope?
- Moving along the diagram:
  - What phase transitions do you go through if you go from point A to point B on the graph?



Phase Diagram Checklist

- Phase diagrams show the lowest free energy phase of a substance at a given temperature and pressure.



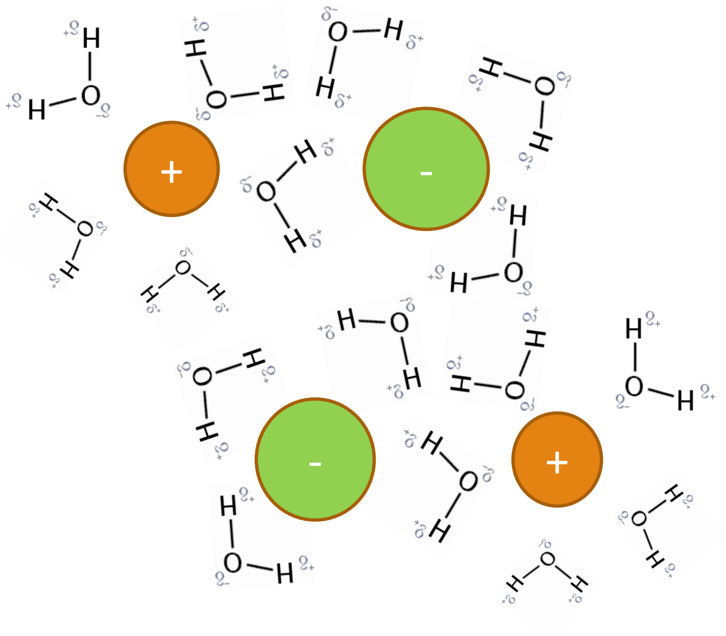
- Identify the key features of the diagram:
  - What is the stable phase at a certain temperature and pressure?
  - Identify the normal boiling point, melting point, etc.
  - Identify the triple point
  - Identify the critical point
  - What phase transition does a specific line represent?
- Moving along the diagram:
  - What phase transitions do you go through if you go from point A to point B on the graph?

Solutions

DEFINITIONS, CONCENTRATION UNITS, LIKE-DISSOLVES-LIKE, ENTHALPY OF A SOLUTION

Introduction to Solutions

- A solution is a homogenous mixture consisting of a solute (can be gas, liquid, or solid) dissolved in a liquid solvent.
- **Whether a solute dissolves in a liquid solvent or not depends on basic thermodynamics: if the solution is more stable than the solute + solvent individually, the free energy of solution will be negative.**



- What does this mean? It means that if you dissolve a solute into a solvent, you are making a solution with a lower free energy.

Enthalpy of Solution

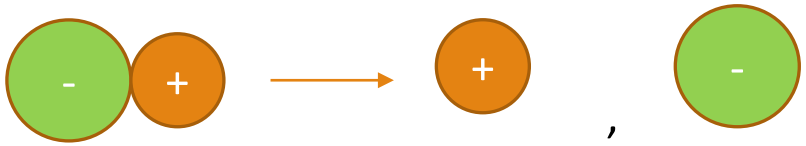
$$\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{solvation}$$

Always +

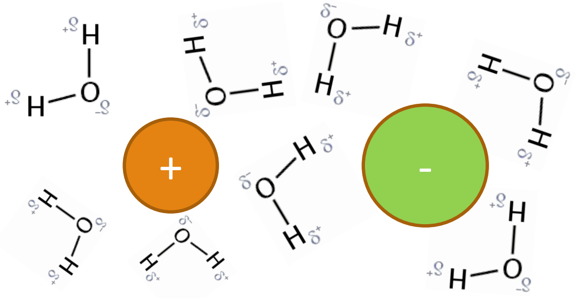
Always -

Step one: Lattice Energy breaks apart ionic compound

Step two: Solvation Energy is released when solvent dissolves positive and negative charges



+



+ $\Delta H_{lattice}$ (positive value)

Bonds breaking = endothermic

+ $\Delta H_{solvation}$ (negative value)

Bonds forming = exothermic

* ΔH solution is 0 for an ideal solution. For your typical salts, it is slightly endothermic. There are plenty of examples of both endothermic AND exothermic solid dissolution processes

Thermodynamics of Solution

Salt Dissolving in Water

$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{solvation}} \approx$ **0***

$\Delta S_{\text{solution}} = S_{\text{(aqueous)}} - S_{\text{(solid)}} =$ **Positive**

$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} =$ **Negative**

$\Delta G_{\text{solution}} = (0^*) - T\,(+)$

Dissolution of salt is typically an entropy-driven process, favored at high temperatures

Gas Dissolving in Water

$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{solvation}} =$ **Negative**

$\Delta S_{\text{solution}} = S_{\text{(aqueous)}} - S_{\text{(solid)}} =$ **Negative**

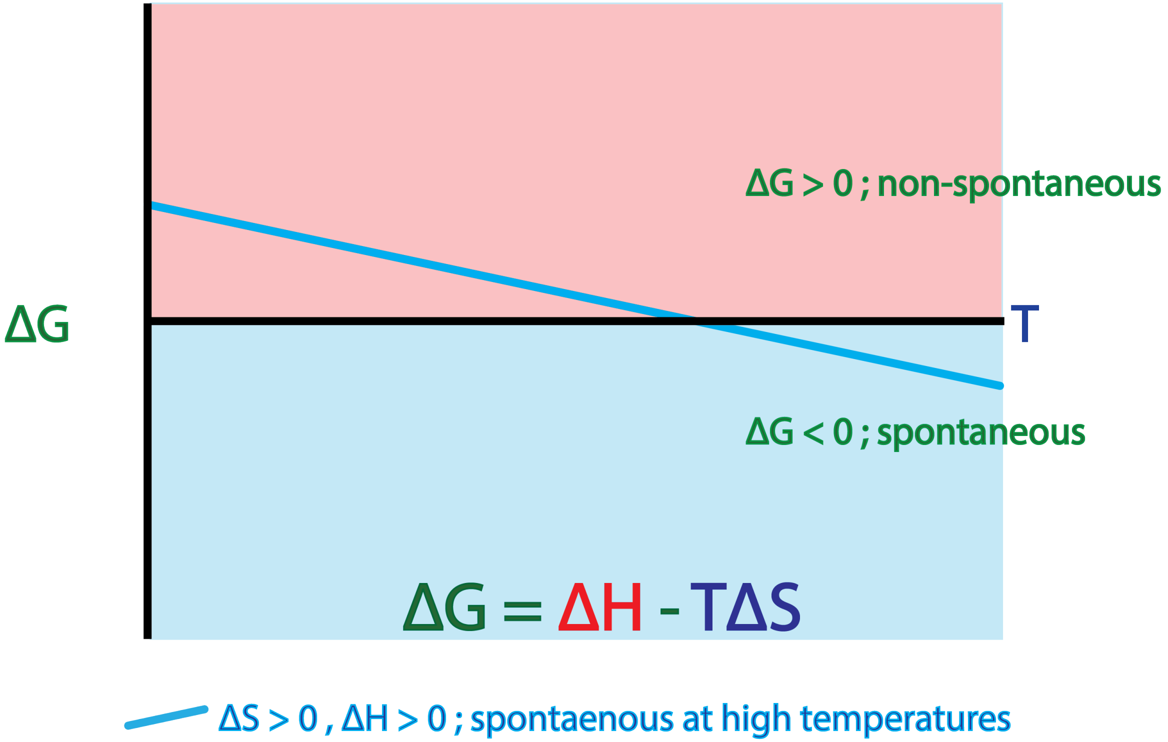
$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} =$ **Negative**

$\Delta G_{\text{solution}} = (-) - T\,(-)$

Dissolution of gas is typically an enthalpy-driven process, favored at low temperatures and high pressures

Free Energy of a Salt Dissolving in Water: $+\Delta H$, $+\Delta S$

- The majority of salts have a positive $\Delta H_{solution}$
- In all cases, the $\Delta S_{solution}$ is positive (solid to aqueous is a positive entropy change)
- **Dissolution is favored at high temperatures for all salts dissolving in water.**

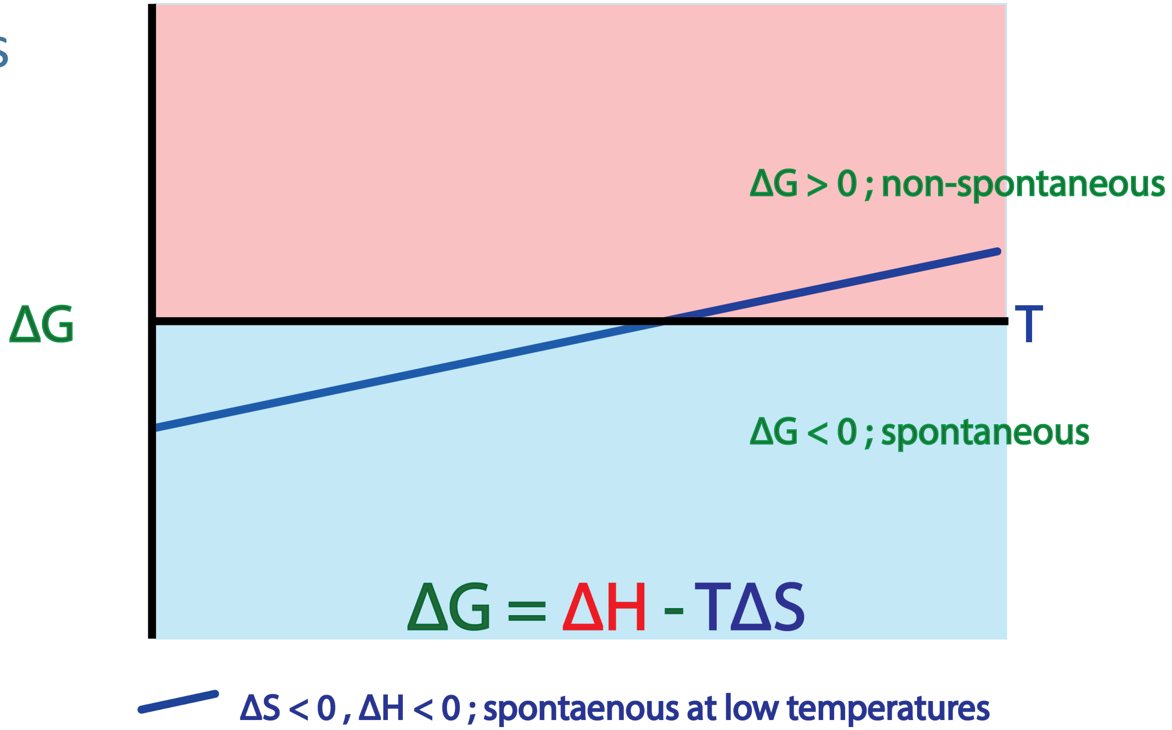


Free Energy of a Gas Dissolving in Water: $-\Delta H$, $-\Delta S$

- For a gas dissolving in liquid, the reaction is exothermic ($\Delta H_{solution} < 0$) because there is no lattice energy and a negative solvation energy.

- There is a negative change in entropy ($\Delta S < 0$) because you are going from gas to aqueous

- Therefore, dissolution is favored at low temperatures. Henry’s Law also states that gas dissolution is favored at high pressures.



Like-Dissolves-Like: Henry’s Law

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process, favored at high temperatures:

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \textbf{Negative}$$

$$\Delta G_{\text{solution}} = (+) - T(+)$$

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process. There are two important points here:

1. **Enthalpy is important when mixing two liquids. Matching the IMF’s of two liquids MINIMIZES the ΔH term.**
2. **Increasing temperature increases solubility**

Dispersion forces:

C_nH_{n+2}, CCl_4, $C0_2$, F_2 etc.

Dipole-Dipole:

CH_2O, CH_3COCH_3, $AsCl_3$, etc.

H-bonding:

CH_3OH, H_2O, HF, NH_3, etc.

Colligative Properties

THE LOWER FREE ENERGY SOLUTION HAS PHYSICAL PROPERTIES REFLECTIVE OF A MORE STABLE LIQUID:

HIGHER BP, LOWER FP, LOWER VP, OSMOTIC PRESSURE

Introduction to Solutions

- Some of the concentration units you should know for solutions are (gchem fundamentals chapter):
  - Molarity (M): moles of solute per liter solution (mol/L)
  - Molality: moles of solute per kilogram solvent (mol / kg)
  - Mole Fraction: moles of a particular species per total moles of solution / mixture (dimensionless)

$$\boxed{M = \frac{moles\ solute}{L\ solution}}$$

$$\boxed{m = \frac{moles\ solute}{kg\ solvent}}$$

$$\boxed{X_A = \frac{moles\ A}{moles\ Total}}$$

Colligative Properties: Units

Can you convert 1.20 m K_2CrO_4 to its effective molarity? MW = 194.2 g/mol

Colligative Property Summary

Vapor Pressure Lowering (Raoult's Law):

- Solves for **the *new, lower* vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A)
  - $P_A = X_A P°_A$

Freezing Point Depression:

- Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (m)
  - $\Delta T_f = i\, k_f\, m$

Boiling Point Elevation:

- Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (m)
  - $\Delta T_b = i\, k_b\, m$

Osmotic Pressure:

- Solves for the pressure exerted by a fluid to achieve physical equilibrium of osmosis against the hydrostatic pressure, based on **the molarity of the solute** (M)
  - $\Pi = iMRT$

$$i = \frac{moles\ of\ particles\ in\ solution}{moles\ of\ solute\ dissolved} = \frac{effective\ concentration}{stated\ concentration}$$

van’t Hoff Factor

- Colligative properties depend on the effective concentration, which can be more than just the stated concentration.
- The reason for this lies in the fact that ΔS is greater for ionic solids that dissociate into more ions, resulting in a greater effect of the colligative property
- We make this “correction” by using the Van’t Hoff Factor (i) in our colligative property calculation
- Colligative properties are dependent on the stated concentration TIMES the i-factor

Which of the following solutions has the same boiling point as 0.6M Sucrose?

a. 0.6 M NaCl

b. 0.2 M Na_2SO_4

c. 0.12 M Fe_3SO_4

Boiling Point Elevation, Freezing Point Depression

- Using the following equations, you are solving for the change in the freezing point or boiling point. **Remember: you are solving for a change (ΔT_f is always negative, ΔT_b is always positive) and you are NOT solving for the final temperatures.**

Freezing Point Depression:

Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (*m*)

$$\Delta T_f = i\ k_f\ m$$

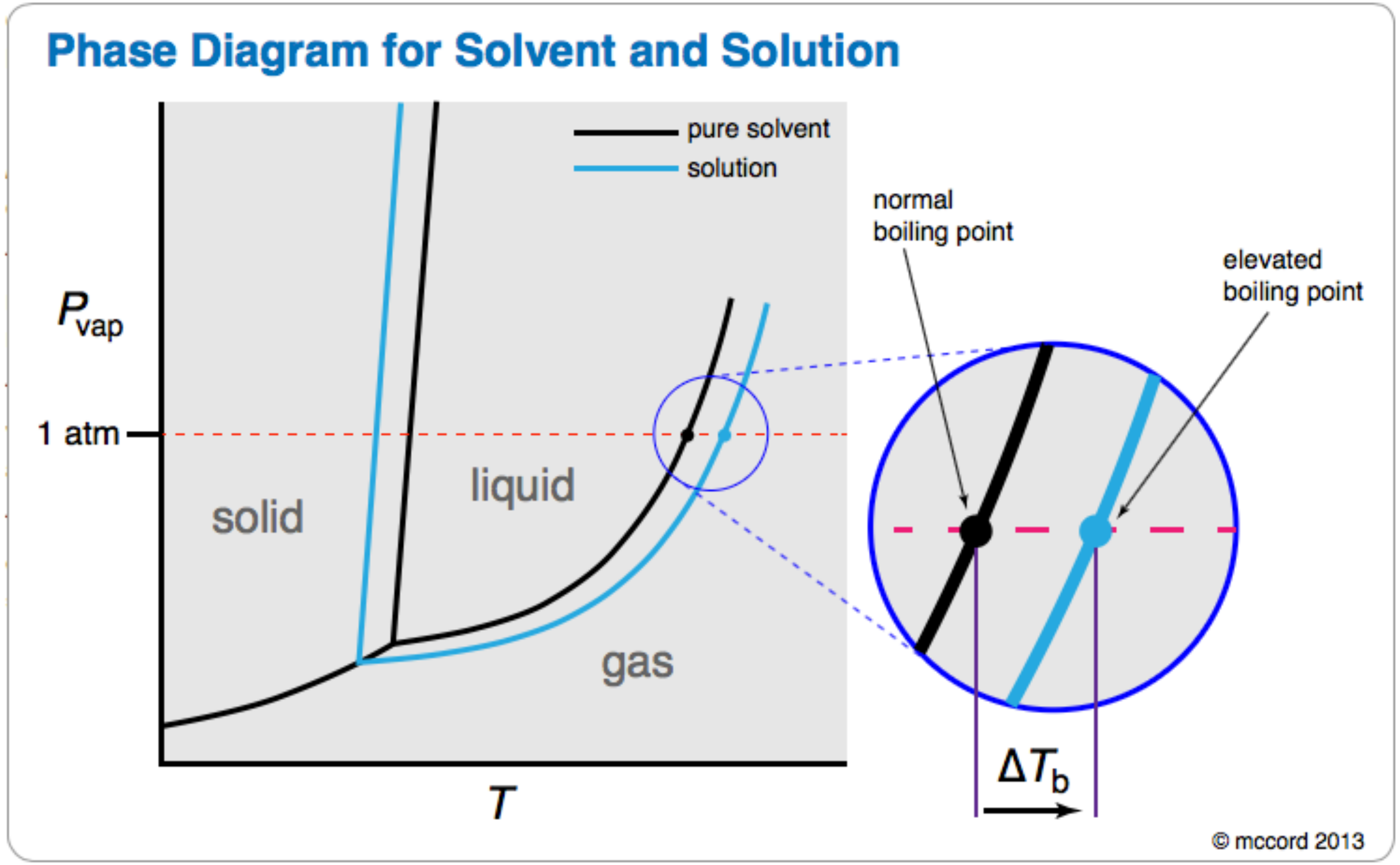
Boiling Point Elevation:

Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (*m*)

$$\Delta T_b = i\ k_b\ m$$

Boiling Point Elevation, Freezing Point Depression

- Creating a solution from a pure solvent lowers the free energy of your substance in the liquid phase.
- This has two effects:
  1. **The freezing point decreases**
  2. **The boiling point increases**
- You can see in the diagram to the right that the liquid phase is favored in a larger range of temperatures



Vapor Pressure Lowering

- Vapor Pressure is **lower when a liquid is more stable**. Therefore, it should make sense that when you create a lower free energy solution from a pure solvent, the vapor pressure goes down.
- **Mathematically, vapor pressure looks like this:**

Vapor Pressure Lowering (Raoult's Law):

Solves for **the *new* vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A) and the vapor pressure of the pure solvent ($P°_A$)

$$P_A = X_A P°_A$$

You WILL have to account for electrolytes in the "total moles" of this mole fraction term, even though you don't see a Van't Hoff Factor here.

Vapor Pressure Lowering – Mixing Volatile Liquids

- The vapor pressure of a binary liquid (A + B) must take into account the vapor pressure of both liquids.
- **Mathematically, this follows Dalton's Law of Partial Pressures:**

Vapor Pressure Lowering (Raoult's Law) + Dalton's Law:

$$P_A = X_A P°_A \qquad P_B = X_B P°_B$$

$$P_{total} = P_A + P_B$$

Vapor Pressure Lowering: Mixing Liquids

- When you mix two miscible liquids, you will get a new vapor pressure value for your solution. There are two ways you might be asked to determine this value.
- Consider two liquids, A and B. Liquid A has a vapor pressure of 200 torr. Liquid B has a vapor pressure of 400 torr. Calculate the vapor pressure when the concentrations of A and B are equal. Then use a vapor pressure diagram to prove your answer.
- What will result is an intermediate between the two vapor pressures

Vapor Pressure Lowering (Raoult's Law):

Solves for **the total vapor pressure**

$$P_A = X_A P^\circ_A$$

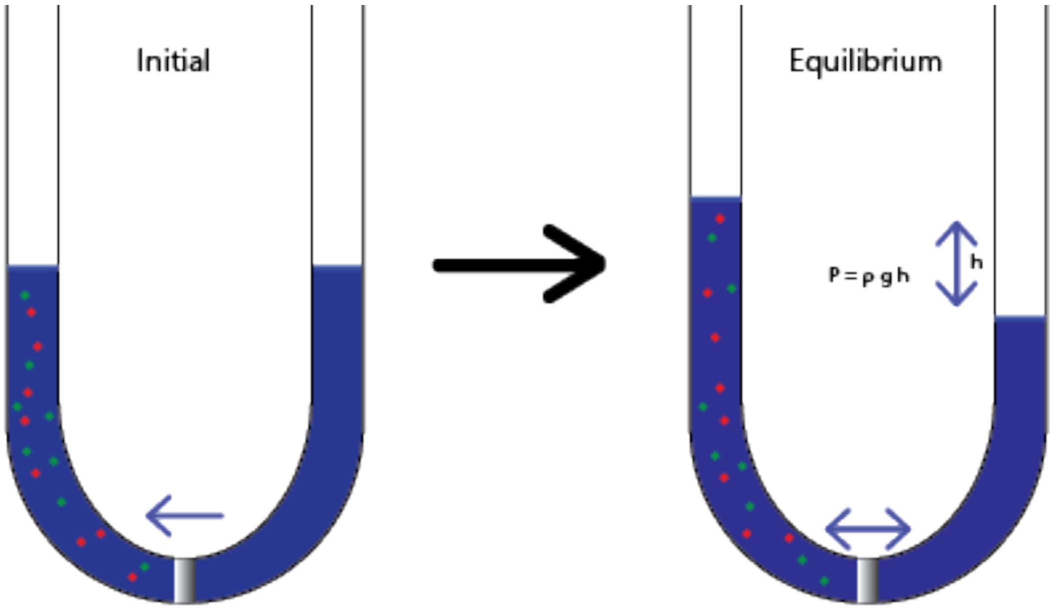
$$P_B = X_B P^\circ_B$$

$$P_{total} = P_A + P_B$$

Dalton's Law (CH301)

Osmotic Pressure

- **Osmotic pressure is the pressure exerted by a fluid to restore osmotic equilibrium.**
- The basic idea is that fluid will flow from the less concentrated to the high concentrated side of a semipermeable membrane (only allows the flow of the solvent; blocks solute).
- Again, this property is due to the fact that the solution is lower in energy. **This is why water flows toward the solution (going from high to low energy).**



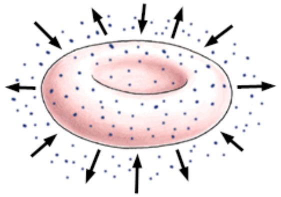
In the initial condition,
the osmotic pressure causes the water to flow from the less concentrated side to the more concentrated side (right to left) in order to dilute

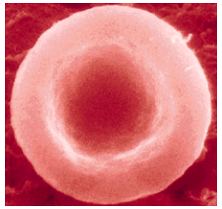
In the equilibrium condition,
the hydrostatic pressure from the atmosphere (pushing to have equal amounts of water on both sides) is balanced by the osmotic pressure (pushing water to the more concentrated side).

$$\Pi = iMRT$$

Osmosis of an Animal Cell

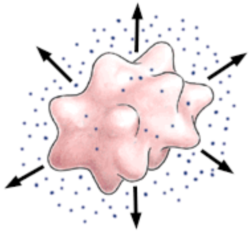
Isotonic Medium: Concentration of solution is the same as in the cell

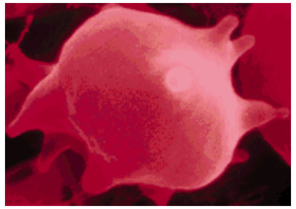




Nothing really happens here

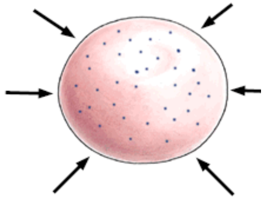
Hypertonic Medium: Concentration of solution is higher than in the cell

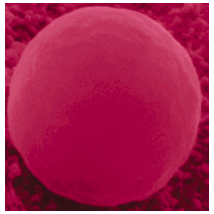




Water escapes the cell, resulting in a shriveled cell body

Hypotonic Medium: Concentration of solution is lower than in the cell





Water enters the cell, resulting in a swelled cell body (might even burst)

Osmotic Pressure – Biological Membranes

- **In biology, osmosis is the process of water flowing from low to high solute concentrations.**
- The driving force of this process is the osmotic pressure and the chemical ion gradient established between the inside and outside of a cell.
- **The direction and outcome of osmosis depends on the ion gradient of the solution:**
  1. **Hypertonic solutions:** high solute concentration on the outside of a cell ; water flows OUT ; results in cells shrinking
  2. **Hypotonic solutions:** high solute on the inside of the cell ; water flows IN ; results in cells swelling
  3. **Isotonic solutions:** equal solute concentrations on the inside and outside of a cell ; no net flow of water ; no change

Colligative Properties: Percent Ionization

All colligative properties can be applied to non-ideal situations arising from:

1. **Ion-pairing**
   - Electrolytes can “find” each other in solution, which lowers the effective concentration. This can only be quantified empirically, when the colligative property has a smaller effect than expected
   - This becomes more common as concentration increases
2. **Weak electrolytes (percent ionization)**
   - A solid dissolves “weakly,” giving a van’t Hoff Factor between 1-2.

$$\text{\% ionization} = (i_{non-ideal} - 1) \times 100\ \%$$

Colligative Properties: Percent Ionization

Chlorous acid ($HClO_2$) is a molecular solute, meaning we should expect that it does not dissociate in solution. However, this is not fully true. A 0.5 *m* chlorous acid solution should have a freezing point of -0.93˚C. In the lab we measure it to be -1.19˚C. This is a result of the fact that chlorous acid partially ionizes into ClO_2^- and H^+.

What is the percent ionization of this 0.5 *m* chlorous acid solution? K_f for water is 1.86 ˚C/*m*

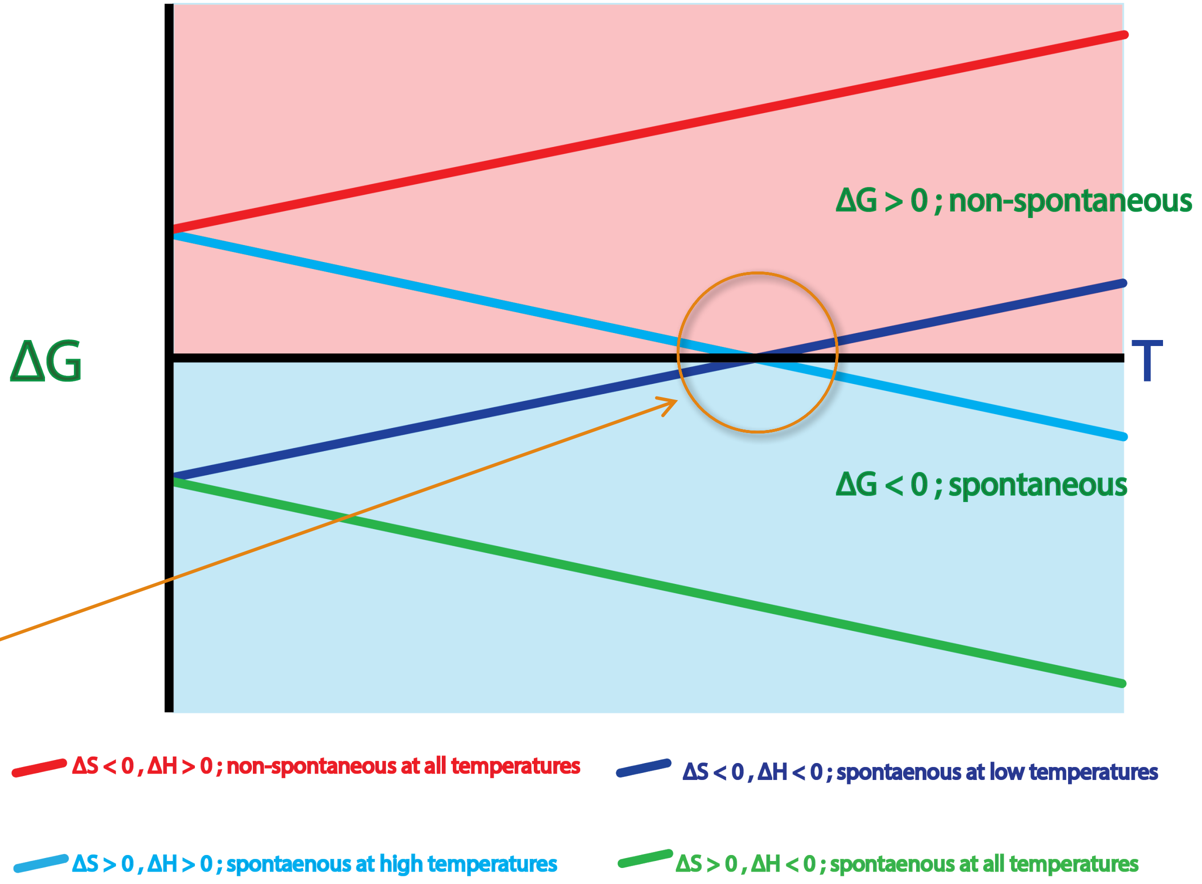
A. 13%
B. 28%
C. 8%
D. 56%
E. None of the above

Additional Slides

Free Energy: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

$$\Delta G = \Delta H - T\Delta S$$



What “Drives” the Phase Change?

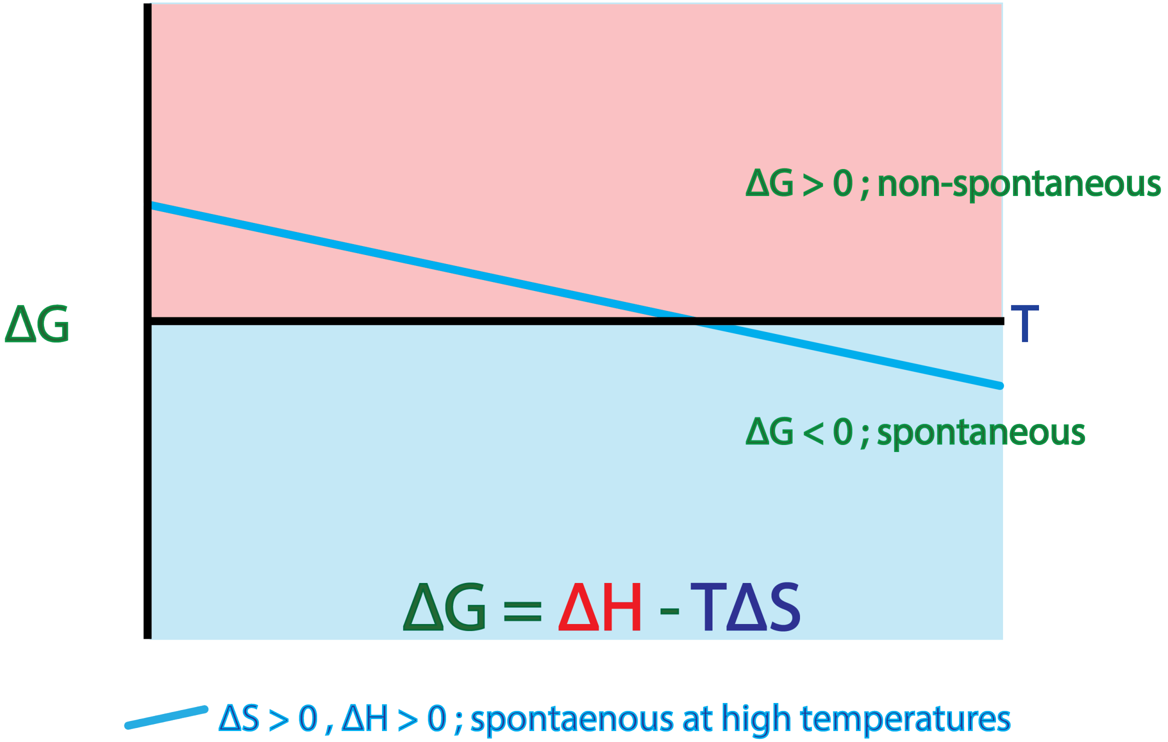
ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

Thermodynamically speaking, the term that “drives” the reaction is the one that is making the ΔG more negative.

$$\Delta G = \Delta H - T\Delta S$$

Free Energy of a Salt Dissolving in Water: +ΔH , +ΔS

- The majority of salts have a positive $\Delta H_{solution}$
- In all cases, the $\Delta S_{solution}$ is positive (solid to aqueous is a positive entropy change)
- **Dissolution is favored at high temperatures for all salts dissolving in water.**



Free Energy of a Gas Dissolving in Water: -ΔH , -ΔS

- For a gas dissolving in liquid, the reaction is exothermic ($\Delta H_{solution} < 0$) because there is no lattice energy and a negative solvation energy.
- There is a negative change in entropy ($\Delta S < 0$) because you are going from gas to aqueous
- **Therefore, dissolution is favored at low temperatures.**